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## (54) ELECTROCONDUCTIVE PASTE AND ITS PRODUCTION

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain an electroconductive paste which can form fine lines and can produce conductor circuits of high quantity and high minuteness by combining a filler of spherical metal powder with a resin satisfying specific conditions.
SOLUTION: In this conductive paste containing (A) spherical metal powder with particle sizes of ≤100μm and (B) a thermosetting phenolic resin as a binder, (C) a polyethylene resin is contained in an amount of 0.01-5wt.% per 100 pts.wt. of the conductive powder. In order to prepare this paste, the component (C) is previously dispersed in a solvent and the component (A) is a copper- alloy powder which is represented by the formula: AgxCuy [$0.001\leq x\leq 0.4$, $0.6\leq y\leq 0.999$ in atomic ratios] in which the silver concentration oil the particle surface is higher than the average concentration in these particles and the particle size is 0.1-100μm.

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CLAIMS

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[Claim(s)]
[Claim 1] the conductive paste which makes a conductive filler spherical metal powder which is the particle diameter of 100 micrometers or less, and uses heat-curing mold phenol resin as binder resin -- setting -- this conductive powder 100 weight section -- receiving -- polyethylene resin -- 0.01 - 5wt% -- the conductive paste characterized by containing.
[Claim 2] The conductive paste according to claim 1 which is expressed with a general formula $Ag_xCu_y$ ($0.001 <= x <= 0.4$, $0.6 <= y <= 0.999$ (atomic ratio)), and is characterized by being copper alloy powder with the silver concentration higher than the silver concentration of an average of a particle on the front face of a particle, and particle diameter being 0.1-100 micrometers as this conductive filler.
[Claim 3] The manufacture approach of the conductive paste characterized by adding the distributed object which distributed polyethylene resin in the solvent beforehand in the manufacture approach of the conductive paste which comes to mix the spherical metal powder which is the particle diameter of 100 micrometers or less, and binder resin and a solvent.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the conductive paste excellent in the fine line plasticity.
[0002]
[Description of the Prior Art] Various conductive pastes are proposed in connection with the rapid progress of electronics, and it is used for various kinds of electronic equipment, electronic parts, and electronic circuitries as an electromagnetic wave shielding application, a jumper application, a through hole application, etc. From the conductive goodness of a metal proper, the conductive paste which uses metal powder as a principal component especially begins the industrial way and the various communication link applications as which high conductivity and high-reliability are required, and is widely used even for the public welfare device. As an electric conduction filler used for these conductivity paste, the shape of an indeterminate mold and resin and spherical powder are used. If the conductive paste using a spherical filler is especially used to the application which needs fine line formation, it is known that good screen-stencil nature will be obtained.
[0003]
[Problem(s) to be Solved by the Invention] However, generally, although it is easy to improve the screen version omission fine line printing, the conductive paste using a spherical filler is one side, the paste after printing tends to spread, and when Rhine spacing is narrow, it has the trouble of being easy to disconnect. This invention offers the conductive paste excellent in the fine line plasticity. That is, the extensive improvement of the fine line plasticity which was the fault of the conventional spherical filler use paste is aimed at.
[0004]
[Means for Solving the Problem] As a result of adding examination variously in order to obtain the conductive paste which was excellent in the fine line plasticity in view of these points, this invention finds out that the conductive paste produced by combining the resin which fulfills a spherical metal powder filler and specific conditions can solve the above-mentioned trouble, and reaches this invention. That is, this invention is as follows.
[0005] 1. the conductive paste which makes a conductive filler spherical metal powder which is the particle diameter of 100 micrometers or less, and uses heat-curing mold phenol resin as binder resin -- setting -- this conductive powder 100 weight section -- receiving -- polyethylene resin -- 0.01 - 5wt% -- the conductive paste characterized by containing.
2. Conductive paste according to claim 1 which is expressed with general formula AgxCuy ($0.001<=x<=0.4$, $0.6<=y<=0.999$ (atomic ratio)), and is characterized by being copper alloy powder with silver concentration higher than silver concentration of average of particle on front face of particle, and particle diameter being 0.1-100 micrometers as conductive filler.
[0006] 3. Manufacture approach of conductive paste characterized by adding distributed object which distributed polyethylene resin in solvent beforehand in manufacture approach of conductive paste which comes to mix spherical metal powder which is particle diameter of 100 micrometers or less, and binder resin and solvent. the case where it is 60micro or less although it is desirable that it is 100 micrometers or less as for the particle size of the metal powder used for this invention -- resolution -- good -- collapsibility -- it is desirable. Although particle size distribution should attain optimization according to the property of each metal impalpable powder, it is desirable to consist of metal powders distributed over various sizes so that it might become the range of particle diameter 100 micrometers or less in this invention.
[0007] For this reason, as for the metal powder of this invention, what was produced by the inert gas atomizing method is desirable. The particle recognized suitable amount existence of the powder produced by the inert gas atomizing method, and particles adhered, and since there was very little so-called satellite structure powder with which the particle

has adhered to a little large particle, the distribution for producing a conductive paste is easy, and it turned out that the pack density of a particle can be raised.

[0008] The following copper alloy powder is the most desirable from a fine line plasticity and a conductive point also in the metal powder produced by these inert gas atomization. Although copper alloy powder is expressed with a general formula AgxCuy (0.001<=x<=0.4, 0.6<=y<=0.999 (atomic ratio)), when oxidation resistance with x [ sufficient by 0.001 or more ] is acquired and it does not exceed 0.4, electromigration-proof nature is good. And the copper alloy powder produced by the inert gas atomizing method in 0.001<=x<=0.4 has the silver concentration higher than average silver concentration on the front face of powder. It can ask for the silver concentration this powder front face and near the front face as surface concentration with a depth [ from a front face ] of about 50A by the X-ray-photoelectron-spectroscopy analysis apparatus. Measurement of average silver concentration can dissolve a sample in concentrated nitric acid, and can use ICP (RF inductive-coupling mold plasma-emission-spectrometry meter). Although the copper alloy powder of this invention has the silver concentration higher than average silver concentration on the front face of powder, the silver concentration on the front face of powder is 1.4 or more times of average silver concentration preferably, and they are 2.5 or more times still more preferably.

[0009] Although measurement of the mean particle diameter of the copper alloy powder of this invention can be measured with a laser diffraction mold particle-size-distribution plan, since especially submicron particle distribution tends to produce an error with a maldistribution, measuring equipment, etc., it can be searched for from the image analysis in an electron microscope. Although producing by the atomizing method is desirable as for the spherical metal powder used for this invention, the inert gas atomizing method by nitrogen gas, argon gas, hydrogen gas, etc. and especially the most desirable thing are the gas atomizing methods by the inert gas containing gaseous helium preferably. The following approaches of this inert gas atomizing method are that example. A metal or an alloy is first dissolved in the end crater which uses high-frequency induction heating in inert gas or a vacuum. Melt is spouted into an inert gas ambient atmosphere from a crucible tip after fusion. the high-speed flow which was made to carry out adiabatic expansion of the inert gas spouted simultaneously compressed, and was generated -- ****** -- **** -- it blows off and metal powder can be produced. It is desirable for activated gas, such as oxygen gas, to be 0.01% or less still more preferably 0.1% or less by desirable gaseous helium atomization especially. Although gaseous helium should just be a high grade, it is the gas presentation with this part suitable also for the mixed gas permuted with nitrogen gas. moreover, the mixing ratio of gaseous helium -- metal powder with particle size distribution with a rate especially suitable for the helium-nitrogen mixed gas of 10 - 99 volume % can be produced, and the high electric conduction circuit of pack density can be formed. It is a industrial very useful means to take into consideration a manufacturing cost, particle size distribution, and a paste property, and to use the helium-nitrogen mixed gas of a suitable ratio.

[0010] perfect, although the shape of a ball acquired by the atomizing method of particle shape is common -- not spherical -- a part -- even if it adds deformation, it does not interfere. Although the metal powder used by this invention will not be especially limited if a property is not spoiled, gold, silver, copper, nickel, and especially those alloys are desirable. Although it will not be especially limited if the copper alloy powder used by invention is extent which does not spoil a property At the time of melting, for example, metals, such as aluminum, Zn, Sn, Pb, Si, Mn, nickel, Fe, Bi, Mo, Cr, Ir, Nb, Sb, B, P, Mg, Li, C, Na, Ba, Ti, In, Au, Pd, Pt, Rh, Ru, Zr, Hf, Y, and La, the powder which may add semimetals and those compounds and is used by this invention -- simultaneously Metals, such as aluminum, Zn, Sn, Pb, Si, Mn, nickel, Fe, Bi, Mo, Cr, Ir, Nb, Sb, B, P, Mg, Li, C, Na, Ba, Ti, In, Au, Pd, Pt, Rh, Ru, Zr, Hf, Y, and La, The powder which consists of semimetals and those compounds may be mixed. Moreover, it is the range which does not spoil a property and it is also possible to replace some copper alloy powder of this invention with copper metal powder or silver metal powder. The copper metal powder used at this time does not need to be atomization powder, for example, may be electrolytic copper powder and chemistry reduced copper powder.

[0011] Various additives and a component are added by the conductive paste ingredient of this invention in addition to the above-mentioned metal powder. Although the metal powder of this invention can obtain a spherical particle by the atomizing method as mentioned above, if suitable classification processes, such as an air-current classifier, are used together as a means to adjust the particle size distribution of metal powder further, the property as a conductive paste ingredient will improve greatly further.

[0012] Although the binder resin used for this invention is heat-curing mold phenol resin, as long as it is extent which does not spoil a property, resin other than heat-curing mold phenol resin may be added. as resin other than heat-curing mold phenol resin -- an epoxy resin, polyester resin, polyvinyl butyral resin, polyimide resin, polyamide resin, ethyl cellulose resin, urethane resin, and acrylic resin -- one kind -- or two or more kinds can be combined and it can use.

[0013] Although the binder resin used by this invention has desirable 5 - 40 weight section to the conductive impalpable powder 100 weight section, it is 10 - 30 weight section more preferably. Sufficient amount of resin to combine the conductive impalpable powder in the film in below 5 weight sections is hard to be obtained, and when it is below 40 weight sections, conductivity falls. Although the melting point is the range which is 50 degrees C - 150 degrees C, and the polyethylene resin in this binder resin will not interfere with any structures if it can be distributed during a conductive paste, it is desirable that it is in the range whose melting point is 90 degrees C - 140 degrees C. The modified resin which copolymerized no denaturalizing and an oxidization mold part by the acrylic acid or vinyl acetate is sufficient as polyethylene resin. In the case of an oxidation type, it is desirable that the range of the acid number is 5-200mg (KOH/g), and it is more desirable that it is in the range which is 10-120mg. Since sufficient dispersibility is acquired and the homogeneity of the hardening film is acquired when the acid number is in the range which is 5-200mg, it is desirable. It is desirable to make it distribute as a configuration by the shape of a non-solvent wax and the gel which made fine particles swell with a solvent. Although what kind of solvent will not interfere, either, if there is moderate bloating tendency when making it swell with a solvent, it is desirable to make the solvent of an aromatic series system distribute. For example, they are toluene, a xylene, ethylbenzene, t-butyl toluene, a cumene, diisopropylbenzene, dodecylbenzene, etc.

[0014] Although the content of the polyethylene resin in this binder resin is 0.01 - 5wt% to conductive impalpable powder, it is 0.5 - 3wt% more preferably. When resolution good at the time of printing when a content is less than [ 0.01wt% ] is ****** and more than 5wt%, since the conductivity of the hardening film falls, it is not desirable. Although the heat-curing genotype phenol resin in this binder resin will not interfere with any structures if it is a heat-curing mold, it is desirable that the range of the mole ratio of formaldehyde/phenol is 1-2. As for the weight average molecular weight of this heat-curing mold phenol resin, it is desirable that it is 300-5000, and it is more desirable that it is 1000-4000. The case of less than 300, there are many steams generated at the time of heat hardening, a void tends to be made into the film, and sufficient film reinforcement is hard to be obtained. In an adult case, fusibility is inadequate and pasting becomes difficult from 5000. It does not interfere, even if it transposes a part of heat-curing mold phenol component used for this invention to a compound with other phenolic hydroxyl groups. Alkylphenol resol mold resin using mixture [ with p-cresol or o-cresol ], m-cresol or 3, and 5-dimethylphenol as resin with a phenolic hydroxyl group, xylene resin denaturation resol mold resin, rosin denaturation phenol mold resin, etc. are mentioned. Measurement of weight average molecular weight shall compute the value which carried out gel-permeation-chromatography (GPC) measurement by carrying out styrene conversion.

[0015] In order to raise the dispersibility of the conductive impalpable powder under conductive paste of this invention, an additive may be added for removing or returning the metallic oxide of this conductive impalpable powder front face etc. As an additive, they are nitrogen-containing heterocyclic compounds, such as saturated fatty acid, unsaturated fatty acid, those metal salts, high-class fatty amines, primary amine, secondary amine, tertiary amine, imidazole derivatives, triazoles, and tetrazoles, a titanate organic compound, an organic silicon compound, an organic zirconium compound, an organic phosphorous compound, a hydroquinone and its derivative, a metal chelate formation agent, a phenolic compound, an anthracene and its derivative, and one or more sorts chosen more, for example. The addition of an additive is good to carry out 0.1-25 weight section addition of the one or more sorts of said additive to the conductive impalpable powder 100 weight section. When effectiveness, such as reduction of the effectiveness of an additive, for example, dispersibility, defoaming, and an oxide, does not fully act but said amount of additives exceeds 25 weight sections below in the 0.1 weight section, the property as a paint film, for example, thermal resistance, hardenability, an adhesive property, etc. fall. Preferably, it is 0.1 - 10 weight section.

[0016] It cannot be overemphasized that a well-known viscosity controlling agent, a diluent, a sedimentation inhibitor, a leveling agent, and a coupling agent may be suitably blended with the conductive paste of this invention. In order to improve dispersibility of the conductive impalpable powder under conductive paste of this invention, roll mold kneading machines, such as axis-of-ordinate kneading machines, such as kneading machines for high viscosity, such as a batch kneader, a spiral mixer, a planetary mixer, a pony type mixer, and a butterfly mixer, a roll mill, and taper rolls, can be used. In order to fully demonstrate the effectiveness of this invention, it is desirable that the conductive impalpable powder and binder resin under conductive paste are distributing to homogeneity.

[0017] Although especially the substrate used for this invention is not limited, organic substrates, such as inorganic substrates, such as metal substrates, such as ceramic substrates, such as an alumina substrate, a nitriding aluminum substrate, and a glass substrate for low-temperature baking, and aluminum, stainless steel, a glass epoxy resin substrate, a paper phenol resin substrate, a polyimide substrate, a polyester resin substrate, BT resin substrate, the Pori Sall John resin substrate, a polyether ape phon resin substrate, a polyetherimide resin substrate, a polybutadiene-resin substrate, a glass polyimide resin substrate, and a flexible substrate can usually be used for it

[0018]

[Embodiment of the Invention] Hereafter, an example and the example of a comparison explain this invention

concretely. In addition, various trials given in an example were performed as follows.
(1) Carry out etching formation of Rhine (Rhine / tooth-space =200micrometer / 200 micrometers (die length of 100mm)), carry out spreading hardening of the solder resist after that, and consider as a fine line plasticity evaluation substrate at fine line plasticity copper-clad CEM-3 substrate (copper foil thickness of 35 micrometers). The level difference of Rhine/tooth space is formed in about 10 micrometers. this evaluation substrate top -- the stainless steel of the pattern of ten Rhine / tooth-space =200micrometer/200micrometer (die length of 100mm) Rhine numbers -- being clean (180 meshes) -- it used, the conductive paste was screen-stenciled and the fine line was formed. After fine line formation and after leaving it at 25 degrees C for 1 hour, heat hardening of this evaluation substrate was carried out for 20 minutes at 170 degrees C, and it considered as the test sample. The tooth space between each Rhine (a part for a crevice) is measured, the average is calculated, and the percentage reduction of a tooth space is calculated. Let this be fine line nature. Fine line nature judges what is 70% or more that fine line nature is good. Tooth-space spacing was measured using the laser focus displacement gage. The conductivity of each Rhine was measured using 4 terminal method, the average was calculated, and it considered as fine line resistance.
[0019] The production approach of the copper impalpable powder used for an example and the example of a comparison and copper alloy impalpable powder is shown below.
(2) 330g of production copper grain children of copper impalpable powder was dissolved using high-frequency induction heating in the graphite crucible. The ambient atmosphere was permuted by gaseous helium and operated. It blew off from the nozzle (it equips in the shape of [ 18 ] a periphery with 1.2mm of diameters of a nozzle) which attached the gaseous helium of pressure 30 k/G in the shape of a periphery to the melt which falls from a crucible tip after heating to 1600 degrees C, and copper powder was produced. Uptake of the obtained powder was carried out with the cyclone. When the obtained copper powder is observed with a scanning electron microscope, particle size calls powder 20 micrometers or less copper impalpable powder among the copper powder which might be spherical (it was 15.0 micrometers in mean particle diameter.).
(3) Copper/silver alloy powder was completely produced on the same conditions with the above (2) using 316g of production copper grain children and 15g of silver granule children of copper alloy powder. The surface silver concentration of the obtained copper/silver alloy powder was measured by the X-ray-photoelectron-spectroscopy analysis apparatus. In order that measuring beam electronic energy may compare with measurement of silver concentration according to near peaks, Ag3d 5/2 (K alpha rays of aluminum) and Cu3p (K alpha rays of Mg) are chosen, and it is a front face. It asked as about [ depth 50A ] surface concentration, and the ratio of the average silver concentration for which it asked by this value and ICP was made into the silver ratio of concentration. The silver ratio of concentration was [ 9.6 micrometers and the maximum grain size of mean particle diameter ] 60 micrometers in 4.5. Particle size distribution measured and asked for grain size from the SEM photograph. Particle size calls powder 20 micrometers or less copper alloy impalpable powder among the obtained copper alloy powder.
[0020]
[Example 1] Polyethylene resin A0.5g and triethanolamine 0.1g in 100g of these copper impalpable powder, 8g (for a phenol / formaldehyde ratio, weight average molecular weight is phenol resin of 1000 at 1.0) of heat-curing mold phenol resin, and Table 1, and dipropylene glycol methyl ether 10g were kneaded with 3 rolls, and the conductive paste was produced. When the obtained conductive paste was applied like the above (1) and fine line resistance was measured, they were 1.8 ohms and a good value. When fine line nature was evaluated, they were 80% and a good value.

[0021]
[Example 2] After stirring for 1 hour and making it fully distribute, having mixed polyethylene resin A10g in Table 1 with xylene 40g, and heating at 70 degrees C, it cooled radiationally to 25 degrees C and the wax-like polyethylene resin distribution object was produced. 100g of these copper impalpable powder, and 8g (for a phenol / formaldehyde ratio, weight average molecular weight is phenol resin of 1000 at 1.0) of heat-curing mold phenol resin -- this -- polyethylene resin paste A2.5g and triethanolamine 0.1g, and dipropylene glycol methyl ether 10g were kneaded with 3 rolls, and the conductive paste was produced. When the obtained conductive paste was applied like the above (1) and fine line resistance was measured, they were 1.6 ohms and a good value. When fine line nature was evaluated, they were 93% and a good value.
[0022] Examples 1-7 and the examples 1-3 of a comparison were produced like the following. The polyethylene resin used at that time is shown in Table 1. A result is as being shown in Table 2. The conductive paste of this invention shows the fine line property of having excelled very much so that clearly from Table 2.
[0023]
[Table 1]

| ポリエチレン樹脂 | 融点（℃） | 酸価（ＫＯＨ／ｍｇ） |
|---|---|---|
| A | １０２ | １６ |
| B | １３７ | ２５ |
| C | １４０ | １６ |
| D | ８５ | １４ |
| E | １１０ | － |

[0024]
[Table 2]

| 配合 | 実施例１ | 実施例２ | 実施例３ | 実施例４ | 実施例５ | 実施例６ | 実施例７ | 比較例１ | 比較例２ | 比較例３ |
|---|---|---|---|---|---|---|---|---|---|---|
| 銅合金微粉末（ｇ） |  |  |  | １００ | １００ | １００ | １００ |  |  |  |
| 銅微粉末 | １００ | １００ | １００ |  |  |  |  | １００ | １００ | １００ |
| ポリエチレン樹脂（ｇ） | Ａ | Ａ | Ａ | Ｂ | Ｃ | Ｄ | Ｅ | － | Ａ | Ａ |
| 固形分 | ０．５ | ０．５ | ３．８ | ０．０２ | １．５ | ０．９ | ０．６ |  | ７ | ０．００５ |
| 添加方法 |  | 分散物 |  |  |  |  |  |  |  |  |
| フェノール樹脂（ｇ）<br>固形分 | ８ | ８ | １５ | １０ | １０ | １２ | １４ | １０ | １２ | ９ |
| ファインライン抵抗値（Ω） | １．８ | １．９ | ２．２ | ０．９ | １．０ | ０．７ | ０．８ | １．９ | １５<br>× | ２．０ |
| ファインライン性（％） | ８０％<br>○ | ９３％<br>○ | ８９％<br>○ | ７７％<br>○ | ８７％<br>○ | ８２％<br>○ | ８０％<br>○ | ５１％<br>× | ６５％<br>× | ５２％<br>× |

（注）溶剤としてジプロピレングリコールメチルエーテルを１０ｇ使用している。

[0025]
[Effect of the Invention] as explained above, this invention is possible in fine line formation -- carrying out -- a quality and high definition conductor -- manufacture of a circuit is enabled.

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[Translation done.]